

ANAEROBIC DEGRADATION OF LINEAR ALKYLBENZENE SULFONATE IN FLUIDIZED BED REACTOR

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Abstract - An anaerobic fluidized bed reactor was used to assess the degradation of the surfactant linear alkylbenzene sulfonate (LAS). The reactor was inoculated with sludge from an UASB reactor treating swine wastewater and was fed with a synthetic substrate supplemented with LAS. Sand was used as support material for biomass immobilization. The reactor was kept in a controlled temperature chamber (30±1 °C) and operated with a hydraulic retention time (HRT) of 18 h. The LAS concentration was gradually increased from 8.2±1.3 to 45.8±5.4 mg.L⁻¹. The COD removal was 91%, on average, when the influent COD was 645±49 mg.L⁻¹. The results obtained by chromatographic analysis showed that the reactor removed 93% of the LAS after 270 days of operation.

Keywords: Sand; Biodegradation; LAS; HPLC; Surfactant.

INTRODUCTION

Linear alkylbenzene sulfonate (LAS) is a surfactant used worldwide in detergent production and is present in domestic and industrial wastewaters. Its presence in wastewater treatment plants may result in some problems, such as foaming and inhibition of microorganisms that degrade organic matter, implying a decrease in treatment efficiency.

LAS degradation has been widely studied in aerobic systems, in which removal efficiencies of up to 97% have been achieved (Brunner et al., 1988). However, in anaerobic systems, studies are recent, since LAS has been reported to be recalcitrant under these conditions. Removal of 35% has been achieved in a horizontal anaerobic immobilized biomass reactor (Duarte et al., 2008) and 85% in an UASB reactor (Sanz et al., 2003) for concentrations of 14 mg.L⁻¹ and 4 mg.L⁻¹, respectively.

The anaerobic fluidized bed reactor with immobilized biomass has been widely used for the biological treatment of wastewater. It achieves high efficiency with relatively low hydraulic retention times (Amorim et al., 2009). This reactor configuration favors the retention of high biomass concentration, substantially reducing the area and volume required for removal efficiency and, consequently, increasing the organic matter removal (Saravanan and Sreekrishnan, 2006). Different support materials can be used for biomass immobilization, such as sand, activated charcoal, nylon, polystyrene (Martinelli and Silva, 2005), clay, glass beads and others.

Full scale anaerobic fluidized bed reactors are not common (Saravanan and Sreekrishnan, 2006). However, in experiments to produce hydrogen from glucose fermentation in this reactor configuration using expanded clay as support material, a

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satisfactory result was achieved ($2.49 \text{ mol H}_2 \cdot \text{mol}^{-1}$ glucose), with 90% glucose consumption for a HRT of 2 hours (Amorim et al., 2009).

There are few studies of the application of anaerobic fluidized bed reactors for the anaerobic degradation of LAS. Mosche and Meyer (2002) used this reactor to assess the influence of exposure time on anaerobic microorganism inhibition. The aim was not to achieve high LAS removal efficiencies.

In this study, the removal and degradation of LAS in an anaerobic fluidized bed reactor was evaluated. In a previous study, different support materials were tested, such as expanded clay, activated charcoal, glass beads and sand (Oliveira et al., 2007). Sand was the material that most favored LAS degradation; therefore, it was chosen to fill the larger scale reactor used in this study.

MATERIAL AND METHODS

Fluidized Bed Reactor

Anaerobic LAS degradation was evaluated in a reactor with biomass immobilized in sand (1.55 mm in diameter, approximately). The fluidized bed reactor was made of acrylic, measuring 100 cm high by 4 cm in internal diameter and a total volume of

1.27 L. The height of the fluidized bed was approximately 25 cm, so the working volume was 317.5 mL. Along the length of the reactor, 6 collection points were installed for sampling liquid and solid, according to the diagram in Figure 1. The reactor was inoculated with sludge from an UASB reactor treating swine wastewater, was operated at a hydraulic retention time (HRT) of 18 hours. The feed and recirculation flow rates were $70 \text{ mL} \cdot \text{h}^{-1}$ and $77 \text{ L} \cdot \text{h}^{-1}$, respectively.

During the initial stage of operation (14 days), the reactor was kept in closed circuit to immobilize and adapt the biomass to the synthetic substrate. At this stage, 3 L of feed, composed of synthetic substrate and anaerobic sludge (10% v/v) were prepared.

Composition of the Synthetic Substrate

The surfactant used in this study was sodium dodecylbenzenesulfonate (Sigma), also known commercially as LAS, with a purity of 80%. The reactor was fed with a concentration ranging from 8.2 ± 1.3 to $45.8 \pm 5.4 \text{ mg} \cdot \text{L}^{-1}$.

The synthetic substrate was composed of yeast extract ($500 \text{ mg} \cdot \text{L}^{-1}$), sucrose ($80 \text{ mg} \cdot \text{L}^{-1}$), sodium bicarbonate ($400 \text{ mg} \cdot \text{L}^{-1}$), and $5 \text{ mL} \cdot \text{L}^{-1}$ of saline solution ($50.0 \text{ g} \cdot \text{L}^{-1}$ NaCl; $1.4 \text{ g} \cdot \text{L}^{-1}$ $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $0.9 \text{ g} \cdot \text{L}^{-1}$ $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$).

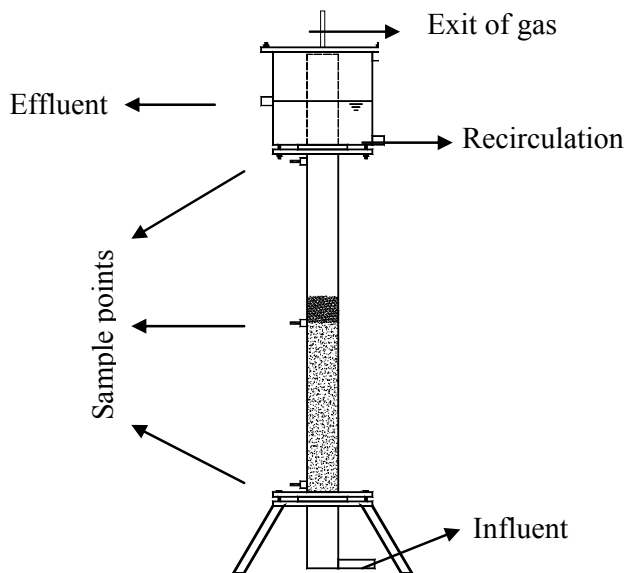


Figure 1: Schematic of a fluidized bed reactor

Chemical and Chromatographic Analysis

Physical-chemical analyses of filtered chemical oxygen demand (COD), sulfate and sulfide were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, 2005). LAS determinations were carried out according to the methodology developed and validated by Duarte et al. (2006). This method employs HPLC (Shimadzu) with a fluorescence detector, a C8 column (Supelco) with gradient elution using methanol and sodium perchlorate (0.075 M) at a 0.5 mL.min⁻¹ flow rate and a temperature of 35 C. The LAS concentration was periodically measured in the liquid phase (influent and effluent) after membrane filtration (0.2 mm) (Duarte et al., 2006).

At the end of the experiment, solid samples (biofilm and media support) were submitted to consecutive washings with methanol in ultrasound during 30 min in order to extract the adsorbed LAS. The extracted material was purified on an ion exchange column (SAX) and concentrated on the C18 column for posterior quantification by HPLC (Duarte et al., 2006). Assays with the support media and sludge for determination of the extraction method efficiency showed that more than 98% of the adsorbed LAS was recovered by extraction.

Determination of the Most Probable Number

This technique was performed at the end of the experiment to quantify the anaerobic microbial groups. The technique consisted of inoculating bacteria from the reactor into a feedstock identical to the reactor feedstock at a LAS concentration of 20 mg.L⁻¹. The bottles (five dilutions from 10⁻¹ to 10⁻¹³) were kept under anaerobic conditions and were incubated at 30°C ± 1°C for 30 days. After this incubation period, growth was found in the following microbial groups: (1) total anaerobic bacteria – presence of turbidity, (2) methanogenic archaea – biogas formation by chromatography and (3) sulfate reducing bacteria – sulfide production, according to the methodology developed by Sakamoto (1996).

The basis of calculation for estimating the MPN was a combination of positive responses. The standard compatibility table (APHA, 2005) was used, which gives the confidence level of 95% for each value determined. The quantification was in MPN.g TVS⁻¹. Analysis of total volatile solids was performed according to APHA (2005).

RESULTS AND DISCUSSION

In the first stage of operation (Stage I), lasting 28 days, the reactor was fed only with synthetic substrate, without LAS. From the analysis of filtered COD, very efficient organic matter removal can be seen, since it remained at 83±3% (Figure 2).

After this period, the second stage of operation (Stage II) was begun with a LAS concentration of 8.2±1.3 mg.L⁻¹ for 28 days. At this stage, the COD influent value was 632±42 mg.L⁻¹ and 86±7% removal (Figure 2) indicated that LAS did not affect the organic matter degradation. The LAS removal was 88±11%, on an average (Figure 3).

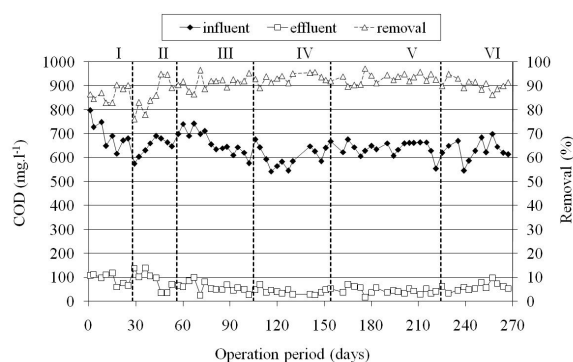


Figure 2: Temporal variation and removal efficiency of filtered COD

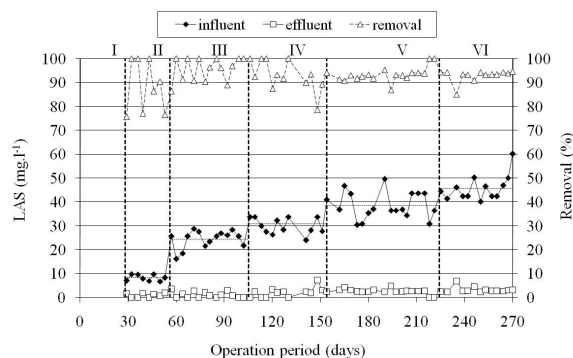


Figure 3: Temporal variation and removal efficiency of LAS

In the next step, lasting 49 days, the LAS concentration in the influent was increased to 24.4±3.7 mg.L⁻¹ (Stage III). At this stage, the COD influent value was 665±50 mg.L⁻¹ and 91±3% removal (Figure 2). The LAS concentration in the effluent was close to zero, maintaining removal values at 96±5% (Figure 3).

After increasing the LAS concentration in the influent to 30.8±4.5 mg.L⁻¹ for 49 days (Stage IV), the system did not show any problem of stability or

decrease in LAS and organic matter removal efficiencies, which remained at $93\pm 2\%$ and $93\pm 6\%$, respectively, for a COD influent of $608\pm 45 \text{ mg.L}^{-1}$.

In the next stages, the LAS concentration was increased to $38.4\pm 5.7 \text{ mg.L}^{-1}$ and $45.8\pm 5.4 \text{ mg.L}^{-1}$ (Stages V and VI, for 70 and 47 days, respectively). In both phases, the LAS removal from the system was $93\pm 3\%$. In this case, the reactor showed excellent biological degradation capacity even at high surfactant concentrations. The organic matter removal in Stage V was $93\pm 2\%$ while in Stage IV the system degraded $91\pm 2\%$ (for a COD influent of $632\pm 42 \text{ mg.L}^{-1}$).

During operation, the reactor received about 7760 mg of LAS and only 510 mg were collected in the effluent. The remainder (93%) was removed from the system by the process of biological degradation. The values of the extraction of LAS in the sand and biofilm, carried out in duplicate at the end of the reactor's operation, were below the detection limit of the calibration curve (0.49 mg.L^{-1}), indicating no adsorption of surfactant on the support and biofilm.

The LAS removal efficiencies achieved with application of the anaerobic fluidized bed reactor were higher than those found in the literature for the systems operated under this condition. Oliveira et al. (2009) and Duarte et al. (2008) obtained removal efficiencies of 28% and 35%, respectively, in a horizontal anaerobic immobilized biomass reactor (HAIB). In a UASB reactor with 4 mg.L^{-1} of LAS influent, Sanz et al. (2003) found removal of 85%. The efficiencies achieved in the work of Oliveira et al. (2009) and Duarte et al. (2008), in addition to degradation, consider the LAS removed by adsorption on the support. However, in this work with the fluidized bed reactor, degradation was therefore obtained without the adsorption of LAS onto biomass and sand.

Probably, the hydrodynamic characteristics of the fluidized bed reactor, which operated by complete mixing and continuous flow, favored LAS removal and degradation, when compared with HAIB and UASB.

Bacteria quantification by MPN showed that the total anaerobic bacteria accounted for $3.98.10^{10} \text{ MPN.g TVS}^{-1}$, while the SRB equaled $3.75.10^9 \text{ MPN.g TVS}^{-1}$, or 9.4% of the total. The value for the methanogenic archaea was $1.93.10^4 \text{ MPN.g TVS}^{-1}$, which represented less than 1% of the total anaerobic bacteria. The difference between the three study groups can be seen in Figure 4.

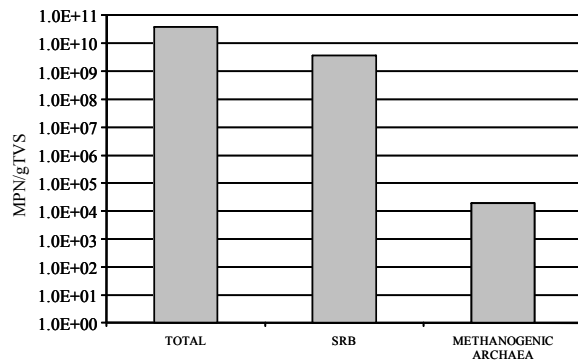


Figure 4: Microbial group

CONCLUSIONS

The reactor was shown to be capable of removing the surfactant LAS, presenting a total efficiency of 93%. It also provided high efficiency of organic matter removal, analyzed in terms of filtered COD (average $91\pm 4\%$), which was not influenced by the presence of LAS. Even at high LAS concentration, the reactor showed good performance as regards COD and LAS removal. Thus, this configuration seems to be the most suitable for LAS degradation in anaerobic systems. The MPN confirmed the presence of sulfate-reducing bacteria and methanogenic archaea, the former comprising 9.4% of the total anaerobic bacteria and the latter less than 1% of the quantified total.

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